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(54) MODIFIED OLEOPHILIC GRAPHITE

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to modified oleophilic graphite, more particularly it relates to oleophilic graphite having polymers adsorbed on the surface.

Oleophilic graphite is prepared by grinding a natural or synthetic graphite below the surface of an organic liquid till a surface area of at least 20 square metres per gram is attained.

Oleophilic graphite preferably has a heat of adsorption of n-dotriacontane from *n*-heptane of at least 700 millicalories per gram and a heat of adsorption of *n*-butanol from *n*-heptane of less than 200 millicalories per gram.

The heats of adsorption can be measured using a Flow Micro-calorimeter as described in Chemistry and Industry 20th March, 1965 p.p. 482.

Preparation of oleophilic graphite by grinding graphite in an organic liquid is described in U.K. Patent 1,168,785.

Oleophilic graphite has the property of thickening lubricating oils into greases and this use of oleophilic graphite is described in U.K. Patent 1,168,784.

In order to thicken a lubricating oil into a grease using oleophilic graphite it is necessary to disperse the oleophilic graphite in the oil, and U.K. Patent Application 15980/67 Specification No. 1,220,451 describes a continuous method of forming a grease.

We have now found that oleophilic graphite can be rendered more easily dispersible in lubricating oils by adsorbing on its surface certain polymers.

According to the invention there is provided a modified oleophilic graphite having adsorbed on its surface a substantially straight chain polymer.

The invention also provides a lubricating composition which comprises a mineral or synthetic base oil containing a modified oleophilic graphite as above.

By substantially straight chain polymer is meant a polymer having a major proportion of its backbone composed of carbon atoms, the carbon atoms in the backbone being unsubstituted or substituted by one methyl substituent. More preferably there are no substituent groups present.

Preferably the modified oleophilic graphite contains less than 2% weight of the straight chain polymer. Though with higher molecular weight polymers e.g. above a molecular weight of 500,000 more polymer may be present e.g. less than 5% by weight. Preferably not enough polymer is present to form a polymer monolayer on the graphite.

As other polymers can affect the properties of the graphite in a different way to straight chain polymers it is possible to have other polymers present in the modified oleophilic graphite.

Both natural and synthetic graphite are well-known and readily available. The synthetic material is, for example, produced from petroleum coke by heating to from 1000° to 3000°C in a vacuum or inert gas. Typically it contains from 95 to 100% wt. carbon. The natural material may have a slightly lower carbon content than this and usually has a larger crystal size.

Oleophilic graphite can be obtained by grinding in organic liquids but it is desirable to use one the bulk of which can be easily removed from the oleophilic graphite. Those

liquids distilling below 500°C and having a viscosity below 600 centistokes at 100°F (38°C) are therefore preferred. Liquids having a surface tension below 72 dynes/cm., preferably from 10 to 40 dynes/cm., at 25°C are preferred.

Suitable organic liquids are hydrocarbons, including straight-chain or branched-chain saturated or unsaturated aliphatic, saturated or unsaturated, substituted or unsubstituted, cycloaliphatic and substituted or unsubstituted aromatic compounds preferably containing up to 10 carbon atoms. Examples of such compounds are n-heptane, octene-2,2,2,4-trimethylpentane, cyclohexane, benzene or toluene. Branched chain aliphatic compounds are particularly preferred. Other suitable organic liquids are paraffinic hydrocarbons obtained by distillation of petroleum e.g. white spirit and also those compounds which contain fluorine, chlorine, or phosphorus and chlorine, for example, carbon tetrachloride.

Other suitable organic liquids are the polar oxygen compounds such as isopropyl alcohol. Silicone fluids can also be used.

For best results, the amount of graphite in the graphite/organic liquid mixture should not exceed 50% wt; preferably it should be from 2—20% wt.

The grinding may be carried out in any suitable grinding mill or device and grinding is continued until an oleophilic graphite having a surface area (as determined by nitrogen adsorption) of at least 20, preferably at least 30, square metres per gram is obtained. Usually this can be achieved by grinding at normal temperatures for the required period but the temperature of the mixture may be artificially increased if desired, for example, up to 400°C. In this case, liquids which have viscosities up to 600 centistokes at 100°F (38°C) may be used, for example, mineral lubricating oils, ranging from "spindle" oils to "bright stocks".

One of the quickest and most effective techniques is to carry out the grinding in a vibratory ball mill.

Air preferably is excluded so far as possible during the grinding operation and this can be most easily achieved by filling the mill with the organic liquid first, followed by the balls and graphite. A suitable procedure is to fill the mill with liquid, add half the balls, then the graphite and finally the rest of the balls. Alternatively a continuous circulating process can be used in which the grinding chambers are full of grinding liquid during the grinding.

When using a ball mill, it is of course desirable to use balls made of a material which does not react with the graphite and which does not wear unduly during the grinding. Vibratory ball mills usualy contain steel balls and these are suitable for the present purpose. It is preferred to use a hard grade of steel for the balls.

A magnetic filter can be used to remove small steel particles from the slurry. A circulatory system can also be used wherein the slurry is pumped through an external magnetic filter and then returned to the mill.

A suitable vibratory ball mill is sold under the trade name "Megapact", Registered Trade Mark manufactured by Pilamec Limited. The grinding effect is produced by the impact of the balls upon the graphite and upon each other, and the casing.

The slurry of oleophilic graphite can be separated from the balls by sieving or by displacement by another liquid and sieving.

As in vibratory ball mills, the greater the energy of grinding the higher the adsorptive capacity for long chain hydrocarbons and the greater the oleophilic properties of the compound the higher energy vibratory ball mills and lower viscosity grinding fluids are preferred.

Preferred vibratory ball mills having an amplitude of vibration of at least 2 mm and preferably more than 3 mm and a frequency of vibration of at least 1500 preferably at least 2500 vibration/min. Most preferably an amplitude of vibration of 4 mm is used.

Preferred grinding liquids used in vibratory ball mills have a viscosity at 100°F (38°C) of less than 30 centistokes, more preferably less than 3 and most preferably less than 1.

The polymers which are used in the present invention are preferably olefin polymers prepared by the polymerisation of the monomer using a Ziegler catalyst. The Ziegler catalysts give rise to a straight chain polymer with virtually no chain branching. The preferred polyolefins are polyethylene, polypropylene and copolymers thereof.

Other polymers that can be used are substituted polyolefins such as polyvinyl chloride and polyvinyl acetate.

Preferably the polymers used have a molecular weight of at least 10,000 and more preferably have a molecular weight of at least 25,000.

Preferably the modified oleophilic graphite contains less than 1% by weight of the polymer and more preferably contains ½% or less by weight.

The polymer can be added to the grinding liquid before, during or after the grinding. It is preferable to add the polymer to the oleophilic graphite in the grinding liquid after grinding has finished, but before the grinding fluid is removed, though the polymer can be added during grinding.

In order to enable ready adsorption of the polymer on the graphite, the grinding fluid and polymer should preferably be chosen so that the polymer is soluble in the grinding fluid, i.e. a substantially single phase can be formed of polymer and grinding fluid.

In a preferred embodiment of the invention oil is added to the slurry of grinding fluid polymer and modified oleophilic graphite and the grinding fluid filtered off. Preferably less

than 20% by weight of oil, based on the weight of graphite, is added to the grinding liquid/slurry mixture so that all the oil added is adsorbed on the graphite. This embodiment enables a 'dry' graphite which comprises graphite particles surrounded by an oil and polymer coating to be formed. Such a graphite is very readily dispersible in oil. The 'dry' graphite can be easily transported from place to place.

The lubricating base oil used for preparing lubricating compositions according to the invention may be a mineral oil or a synthetic oil.

Suitable mineral oils are refined mineral oils obtained from petroleum, for example, those having a viscosity at 210°F within the range from 2 to 50 centistokes preferably from 4 to 40 centistokes.

Synthetic lubricating oils include organic esters, polyglycol ethers, polyphenyl ethers, fluorinated hydrocarbons, silicate esters, silicone oils and mixtures thereof.

The most important class of synthetic oils are the organic liquid polyesters, particularly the neutral polyesters, having a viscosity at 210°F within the range from 1 to 30 centistokes. The expression 'polyester' is used to mean esters having at least two ester linkages per molecule. The expression 'neutral' is used to mean a fully esterified product. Examples of suitable polyesters include liquid diesters of aliphatic dicarboxylic acids and monohydric alcohols (for example, dioctyl, sebacate, dinonyl sebacate, octyl nonyl sebacate, and the corresponding azelates and adipates), liquid diesters of aliphatic dicarboxylic acids and phenols (for example, those described in U.K. patents 1,059,955, 1,058,906, 1,044,550 and 1,044,883), and more complex polyesters (for example, those described in U.K. patent specifications 666,697, 743,571, 780,034, 861,962, 933,721, 971,901, 986,069, 1,105,965 and in co-pending U.K. patent application 31249/65 Specification No. 1,129,965).

The amount of oleophilic graphite required to thicken the base oil to form a grease will depend on the nature of the oil and the consistency of grease required. For most purposes an amount up to 50% wt, based on the final grease, will be used. However, it is remarkable that oleophilic graphite can thicken oils to provide greases with very useful properties at concentrations as low as from 10 to 20% wt., based on the final grease, and this is the preferred concentration range.

The greases according to the invention have remarkable high Drop Points. When their drop points are measured according to the IP or ASTM standard methods, they are found to be above 400°F; such greases are described as 'infusible' and are difficult to produce by conventional methods. By using carefully selected base oils, for example, synthetic oils with high oxidation and thermal stability, greases having a unique combination of properties can be produced.

It has been found that greases according to the invention respond readily to conventional additives such as antioxidants and, especially for use at temperatures above 140°C, antioxidants can be aded to the greases according to the invention. In certain circumstances it may be advantageous to add dispersants to the graphite either before grinding or after grinding to oleophilic graphite. In this way the dispersion of the oleophilic graphite may be aided. Viscosity index improvers, metal deactivators, anti-corrosion agents etc. can also be added to the greases. Load-carrying additives can also be added to the greases according to the invention.

It is a feature of the present invention that it enables greases to be prepared by the relatively simple means of dipersing the modified oleophilic graphite in the base oil. In order to facilitate the dispersion of the graphite the oil containing the modified oleophilic graphite can be subjected to agitation e.g. by colloid milling. In some cases it will be necessary to heat the oil before dispersing the modified oleophilic graphite in it.

The invention will now be described with reference to the following examples.

Example

Graphite was ground in a vibratory ball mill sold under the trade name Megapact by the Pilamec Co. This mill has an amplitude of vibration of 4 mm and a period of vibration of 3000 vibrations per minute (50 cycles per second).

The grinding chamber was filled with white spirit, the balls and graphite added and the chamber sealed. The grinding continued for 8 hours.

The white spirit plus graphite was separated from the balls in the ball mill, and 0.5% by weight based on the weight of graphite, of a polypropylene formed by polymerising polypropylene using a "Ziegler" catalyst of molecular weight approximately 180,000 added thereto. 12% by weight of BG 160/95 base oil (a solvent refined oil of viscosity 160 Redwood No. 1 secs at 140°F and a viscosity index of 95) was added thereto and the white spirit filtered off then the graphite dried to give a dry graphite.

The above process was repeated using a polyethylene of molecular weight of approximately 400,000 in place of the polypropylene.

The "encapsulated" graphite thus formed was dispersed in some more of the same base oil by stirring at a temperature of 90—110°C, cooled, and greases were formed. The properties of the greases formed using the polypropylene are shown in Table 1, and those using the polyethylene are shown in Table 2.

TABLE 1

Wt. of treated graphite	¼ Scale Penetrations Unworked	Worked 60 strokes	Bleed DTD 825
16%	80	85	9%
17%	83	88	7.5%

TABLE 2

Wt. of treated graphite	¼ Scale Penetration Worked 60 strokes	Bleed DTD 825
15%	86	7.5%

Thus it can be seen that the present invention enables a readily dispersible "dry" oleophilic graphite to be formed which can easily be transported and added to a base oil to form a grease.

WHAT WE CLAIM IS:—

1. Oleophilic graphite prepared by grinding a natural or synthetic graphite below the surface of an organic liquid till a surface area of at least 20 square metres per gram is attained modified by having adsorbed on its surface a substantially straight chain polymer as herein defined.

2. A modified oleophilic graphite as claimed in claim 1 in which the substantially straight chain polymer is a polyethylene, a polypropylene or a copolymer thereof.

3. A modified oleophilic graphite as claimed in claim 1 or 2 which contains less than 5% by weight of the polymer.

4. A modified oleophilic graphite as claimed in claim 3 which contains less than 2% by weight of the polymer.

5. A modified oleophilic graphite as claimed in claim 4 which contains less than ½% by weight of the polymer.

6. A modified oleophilic graphite as claimed in any one of the preceding claims in which the polymer has a molecular weight of at least 10,000.

7. A modified oleophilic graphite as claimed in claim 6 in which the polymer has a molecular weight of at least 25,000.

8. A method of preparing a dispersion of a modified oleophilic graphite as claimed in any one of claims 1—7 in which the substantially straight chain polymer, as herein defined, is added to the organic grinding liquid before, during or after grinding.

9. A method as claimed in claim 8 in which the organic liquid has a viscosity below 600 centistrokes at 100°F, distills below 500°C and has a surface tension below 72 dynes/cm at 25°C.

10. A method as claimed in claim 8 or 9 in which the organic grinding liquid is a hydrocarbon containing from 1 to 10 carbon atoms.

11. A method as claimed in any one of claims 8—10 in which the amount of graphite in the graphite/organic grinding liquid mixture is less than 50% by weight.

12. A method as claimed in claim 11 in which the amount of graphite in the graphite/organic grinding liquid mixture is from 2 to 20% by weight.

13. A method as claimed in any one of the preceding claims in which the grinding is carried out in the substantial absence of air.

14. A method as claimed in any one of the preceding claims in which the polymer is a polyolefin.

15. A method as claimed in any one of the preceding claims in which the polymer is a polypropylene, a polyethylene or a copolymer of ethylene and propylene.

16. A method as claimed in any one of claims 8—15 in which the polymer is added to the grinding liquid in an amount of less than 5% by weight based on the weight of graphite.

17. A method as claimed in claim 16 in which the polymer is added to the grinding liquid in an amount of less than 2% by weight based on the weight of graphite.

18. A method as claimed in claim 17 in which the polymer is added to the grinding liquid in an amount of less than 1% by weight based on the weight of graphite.

19. A method as claimed in claim 17 in

which the polymer is added to the grinding liquid in an amount of less than ½% by weight based on the weight of graphite.

20. A method as claimed in any one of the preceding claims 8—19 in which the grinding takes place in a vibratory ball mill.

21. A method as claimed in any one of claims 8—20 in which the polymer has a molecular weight of at least 10,000.

22. A method as claimed in claim 21 in which the polymer has a molecular weight of at least 25,000.

23. A method as claimed in any one of the preceding claims in which a mineral or synthetic lubricating oil is added to the grinding liquid/graphite/polymer mixture.

24. A method as claimed in claim 23 in which less than 20% by weight of the lubricating oil, based on the weight of graphite is added to the grinding liquid/graphite/polymer mixture.

25. A method as claimed in any one of claims 8—22 in which the modified oleophilic graphite is separated from the grinding liquid.

26. A method as claimed in claim 22 or 24 in which the modified oleophilic graphite and at least some of the lubricating oil is separated from the grinding liquid.

27. A method of preparing a modified oleophilic graphite as claimed in claim 1 as herein before described with reference to the Examples.

28. Modified oleophilic graphite prepared by the method of any one of claims 25—27.

29. Lubricating compositions comprising a mineral or synthetic lubricating oil and a modified oleophilic graphite as claimed in any one of claims 1—7 or claim 28.

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